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Understanding and Modifying Cathode / Electrolyte Interfaces

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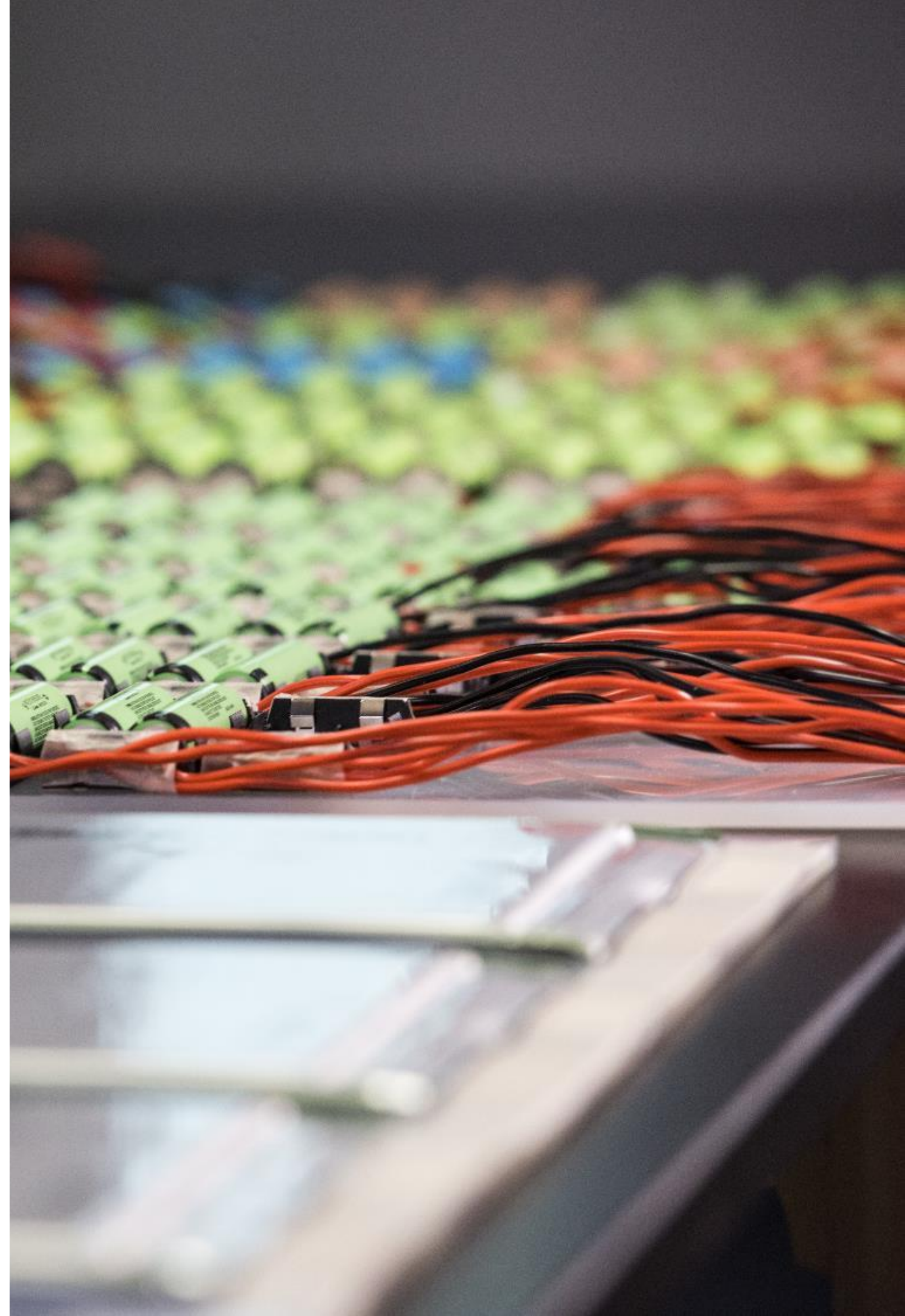
Vehicle Technologies Annual Merit Review

June 12th, 2019

Project ID #bat407



Overview

Timeline

- Start date: Oct. 2018
- End date: Sept. 2021
- Percent complete: 20%

Barriers

- Low energy and high cost
- Knowledge gap between materials research and cell-level need of the materials properties

Budget

- Total project funding: $1,350k
  - DOE share 100%
- Funding received in FY19: $450k

Partners

- Enyuan Hu (Brookhaven National Laboratory)
- Chongmin Wang (Pacific Northwest National Laboratory)

Relevance/Objectives

- Overall Objectives
  - Develop cost-effective synthesis approach for Ni-rich and Low-Co single crystal cathode materials that can maximize cell-level energy for advanced Li-ion battery technologies
  - Investigate and tailor cathode/electrolyte interface for extended long-term cycling and reduced gas evolution
- Objectives this period
  - Synthesis of Ni-rich cathode materials with two different morphologies: single crystalline vs. aggregated polycrystalline
  - Evaluation of Ni-rich cathode at relevant scales
- Impacts
  - Accelerate the development of next-generation Li-ion batteries for future vehicle electrification

Milestones

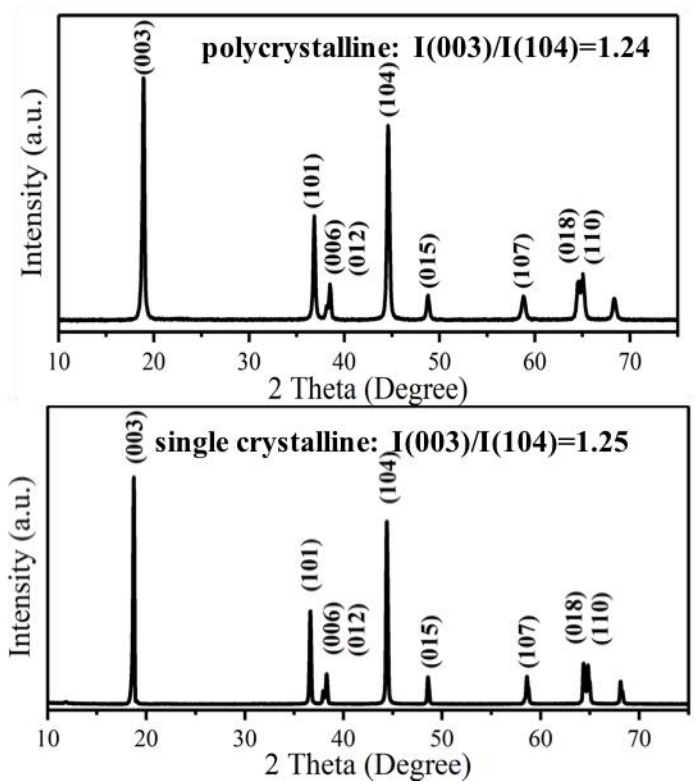
Date	Milestones and Go/No-Go Decisions	Status
December 31. 2018	Q1:Identify the key synthesis parameters for Ni-rich and low-Co NMC cathodes.	Completed on Feb. 14, 2019 (delayed start in Dec.)
March 31, 2019	Q2:Implementation of as-prepared cathode materials into thick electrodes (up to 5 mAh/cm^2).	Completed
June 30, 2019	Q3:Demonstrate >200 mAh/g specific capacity from Ni-rich and low-Co NMC cathodes.	On track
September 30, 2019	Q4:Complete protection of Ni-rich and low-Co NMC by surface coating and demonstrate more than 100 stable cycles in coin cells.	On track

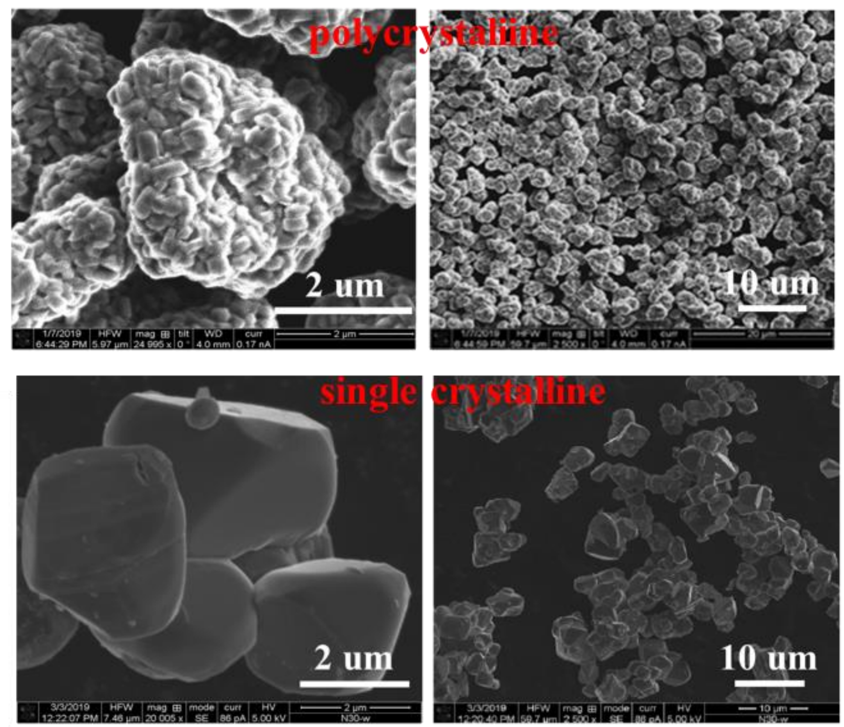
Approach

- Synthesis of Ni-rich and low-Co cathode with different morphologies: polycrystalline vs. single crystalline
- Implementation and evaluation of Ni-rich and low-Co cathode at thick electrode level adaptable by high-energy Li-ion batteries
- Minor Al doping to stabilize lattice structure and modify surface properties of Ni-rich and low-Co cathode to improve cycling stability

Technical Accomplishments

Synthesis of Single Crystalline and Polycrystalline $LiNi_{0.76}Mn_{0.14}Co_{0.1}O_2$ (NMC76)

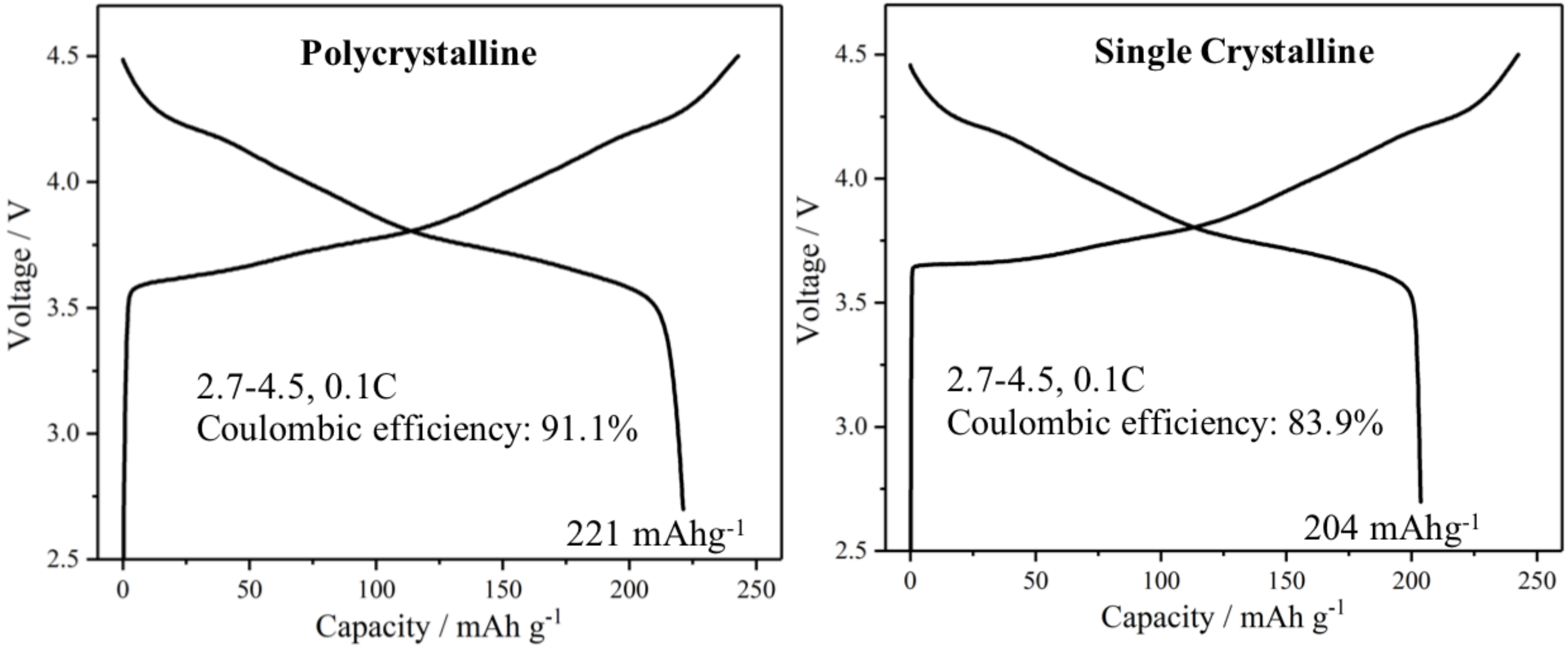




- While polycrystalline is the common form of $LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$, single crystal is preferred for Ni-rich cathode because of reduced gas evolution, reduced sensitivity to moisture, lower surface area and increased tap density.
- Single crystal and polycrystalline NMC76 have been synthesized.
  - Pure phases of α-$NaFeO_2$-type layered structures
  - Similar size at 3-4 µm but polycrystalline NMC76 consists of nano-sized primary particles

Technical Accomplishments

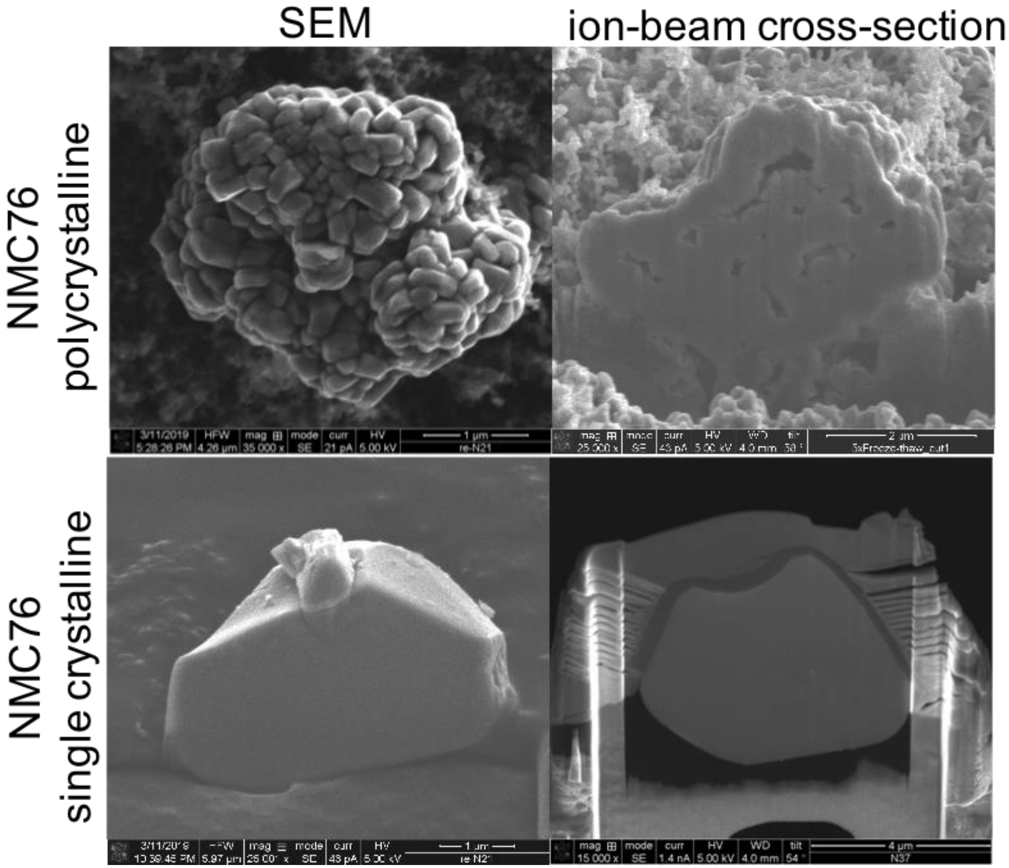
Single Crystalline NMC76 Delivers Greater than 200 mAh/g Capacity



- Only 2% carbon and 2% binder are used for all electrode preparation.
- Single crystalline NMC76 delivers lower capacity than that of polycrystalline ones due to the increased primary particle size.
- Low Coulombic efficiency of single crystal NMC76 indicates the inadequate utilization of active materials.
- Synthesis optimization is needed for NMC76 single crystals.

Technical Accomplishments

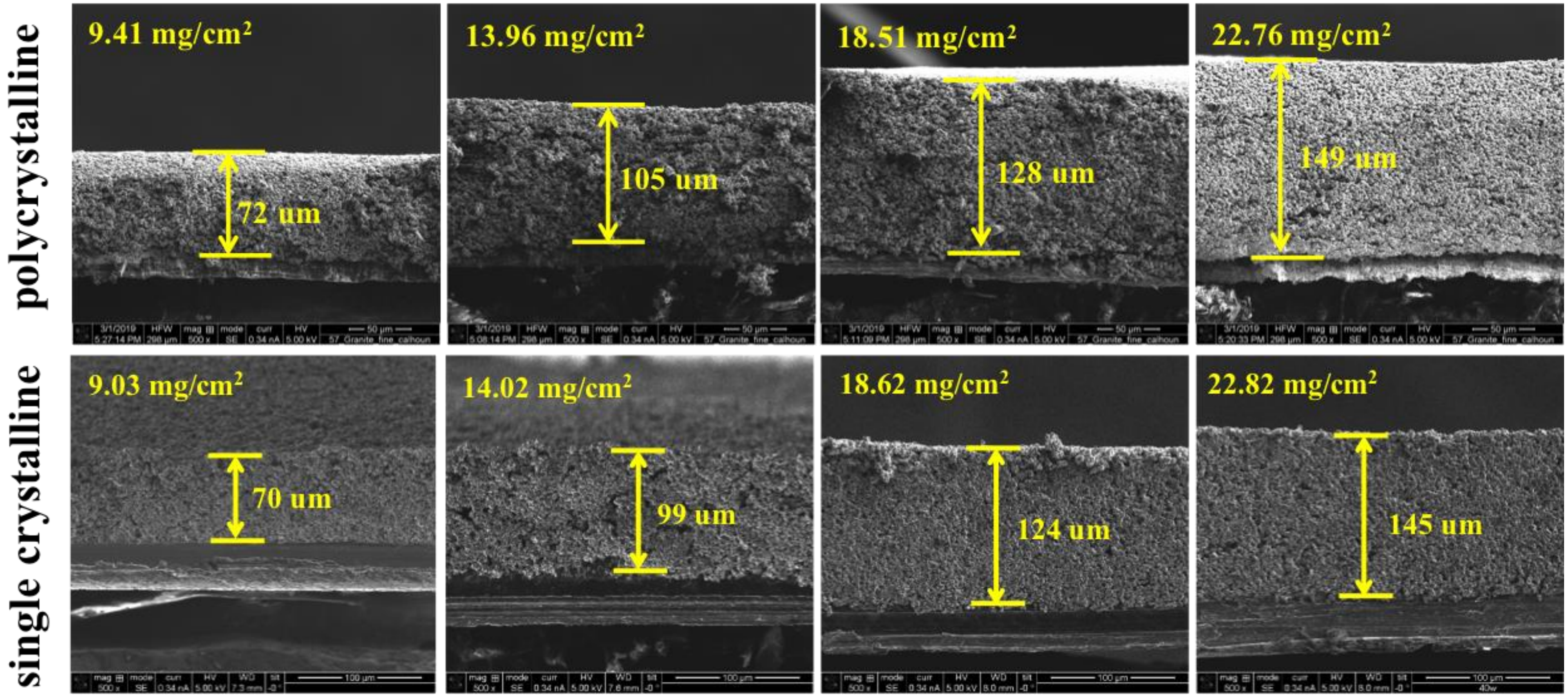
Single Crystalline has Reduced Grain Boundaries



- Each NMC76 polycrystalline is a secondary particle
  - Consists of nano-sized primary particles agglomerated together
  - Internal porosity is observed.
- NMC76 single crystalline is fully dense: No grain boundaries or cracks.

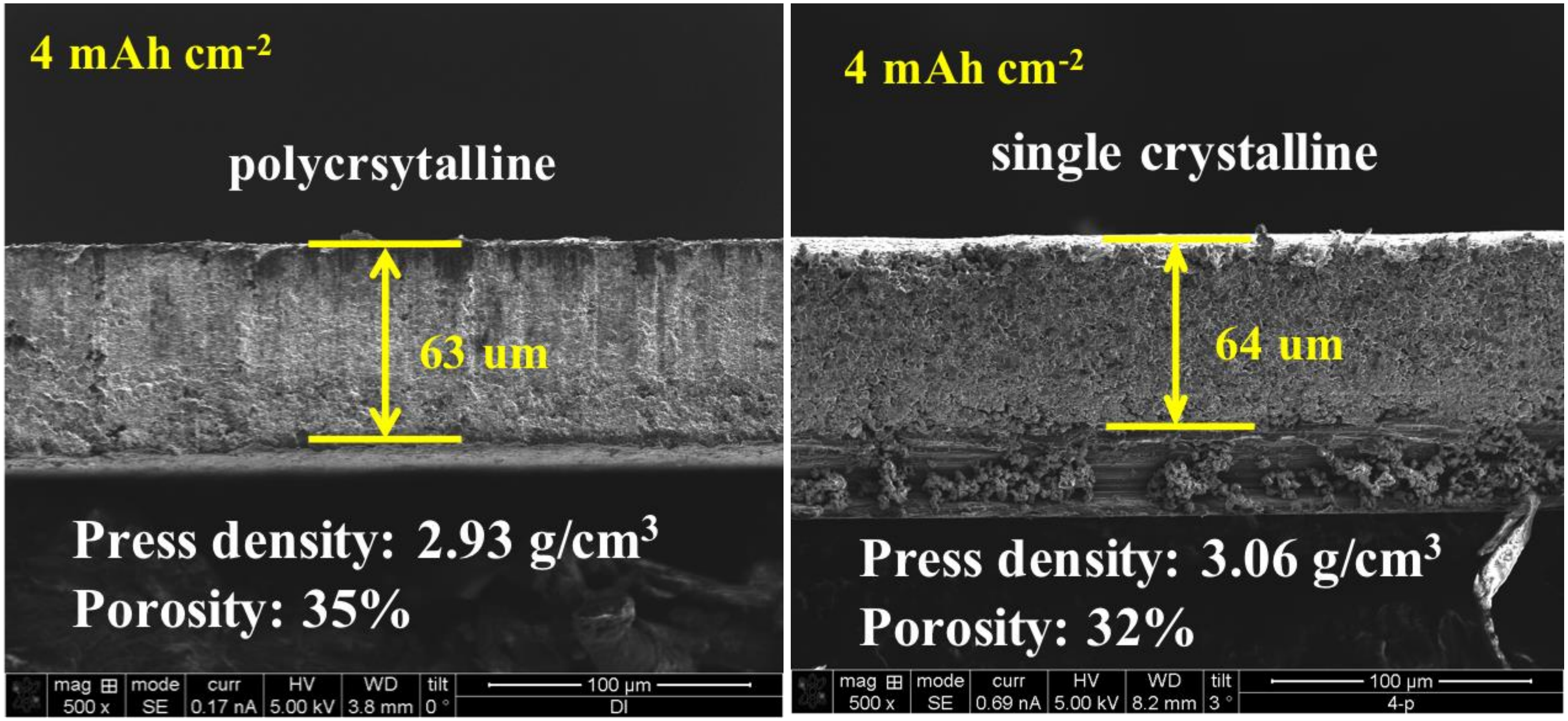
Technical Accomplishments

Single Crystalline NMC76 Allows Dense Particle Packing of Cathodes



- Before calendering: the porosities of polycrystalline and single crystalline-based cathodes are ca.65% and ca.62%, respectively.
- At similar electrode thickness: More active materials can be packed into the cathode in the form of single crystalline.

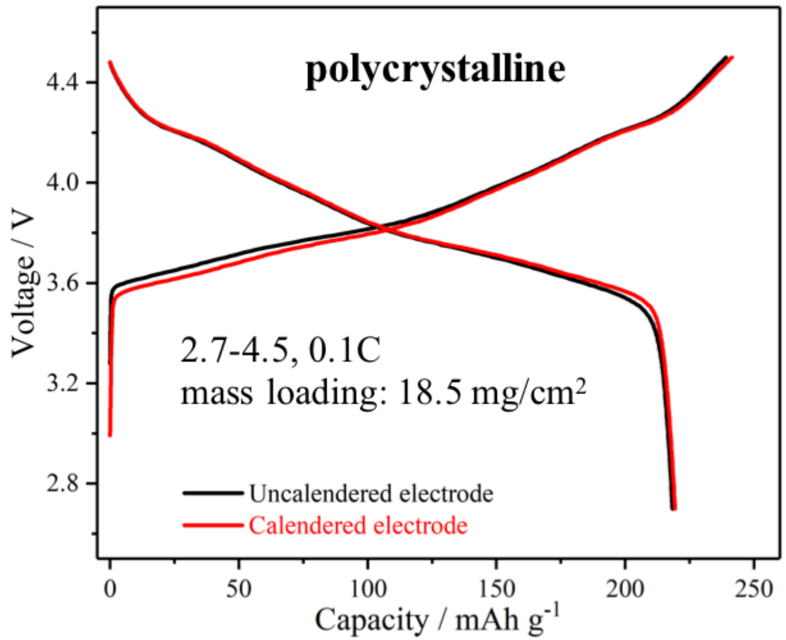
Technical Accomplishments
Calendered Single-Crystalline Cathode is More Compact

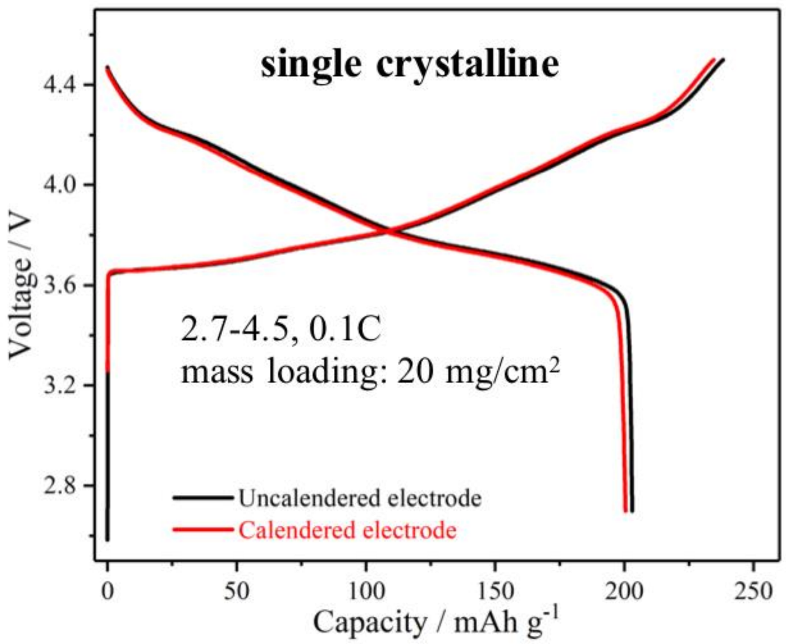


- 4 mAh/cm^2 cathode with 3 g/cm^3 press density: Minimum requirements to construct a 250 Wh/kg Li-ion cell pouch cell (see backup slide).
- Calendered single crystal cathode displays higher press density and lower porosity than those of polycrystalline electrodes: Critical for improving cell-level energy by reducing electrolyte intake

Technical Accomplishments

Good Electrochemical Behavior Observed from Thick Cathodes





- Calendared polycrystalline thick cathodes deliver similar capacity with pristine cathode at ca. 219 mAh/g benefiting from its porous structures.
- Slight capacity decrease (from 204 to 201 mAh/g) is seen after calendering single crystal based cathode probably due to wetting issue.
- The specific capacity of single crystalline NMC76 will be improved through synthesis optimization.

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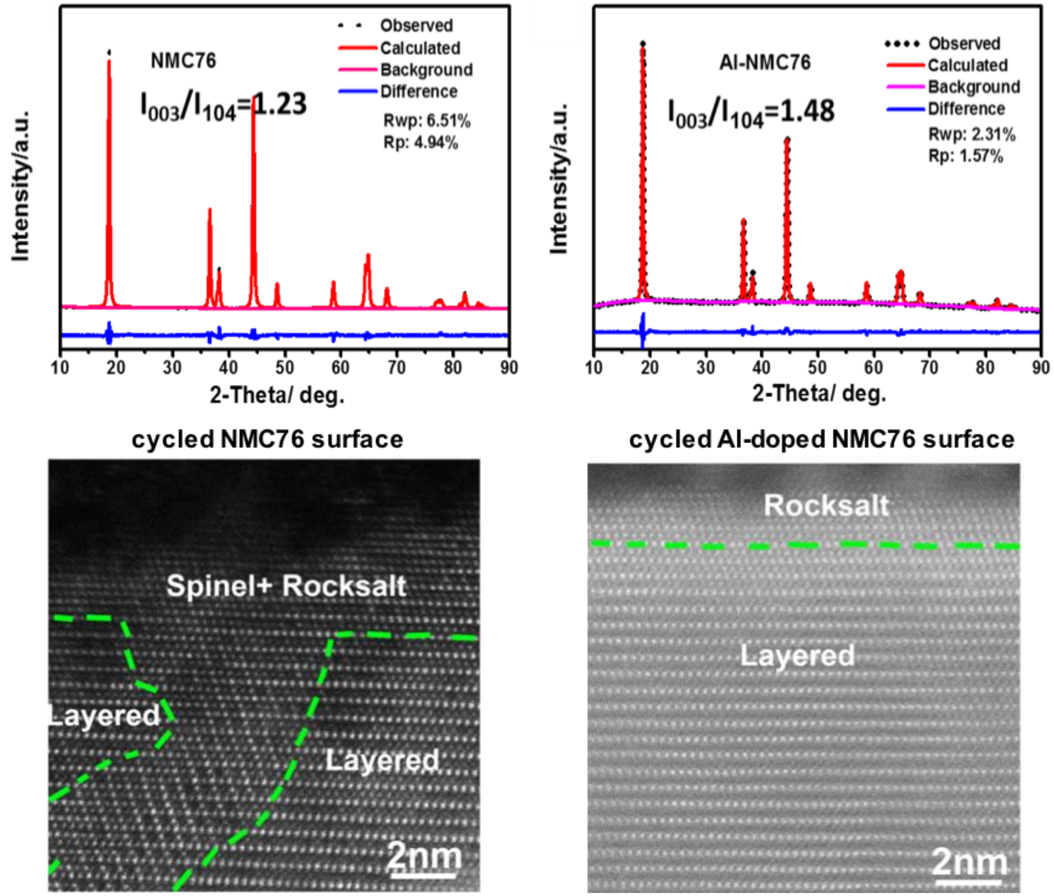
Technical Accomplishments

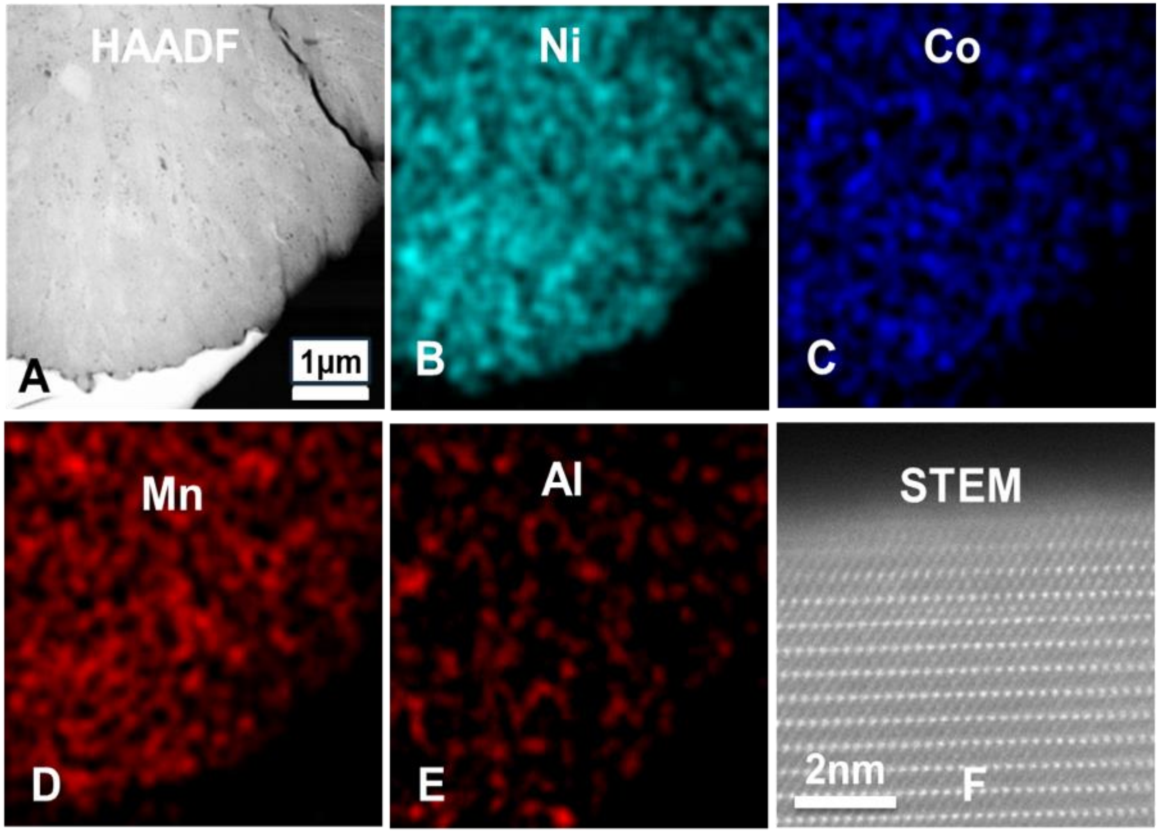
Al-doping Modifies Bulk and Surface Properties



- Al-doping is conducted only on polycrystalline since NMC76 single particle is under synthesis optimization.
- Al-doping of NMC76 (polycrystalline) decreases cation disordering and enhances layered structure integrity: (003)/(104) peak intensity ratio increases after doping.
- Al-doping also mitigates interfacial reactions: reduced amount of rock salt phase on NMC76 surface

Technical Accomplishments

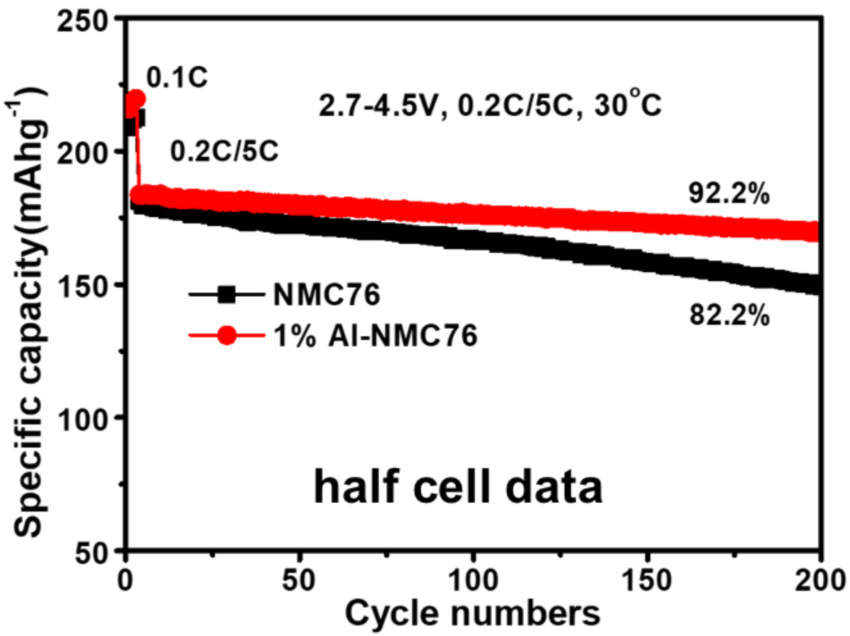
Al-doping is Homogenous within Polycrystalline NMC76

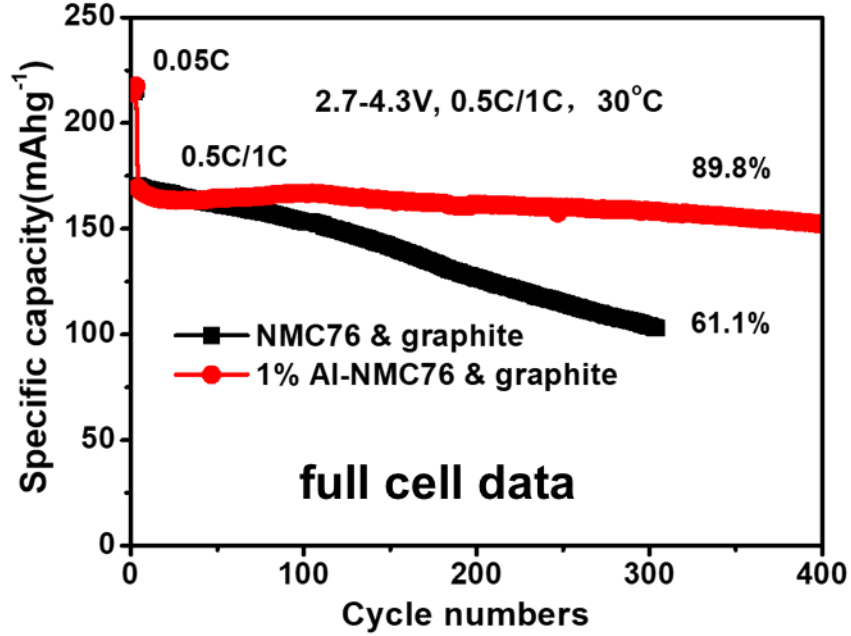


- Al element is homogeneously distributed within polycrystalline NMC76 particles.
- A small amount of Al (oxide) is anchored on the surface as a protective layer.
- Limited Li^{+}/Ni^{2+} cation disorder is found in the layered structure viewed down from R-3m zone axis, consistent with the XRD analysis.

Technical Accomplishments

Preliminary Results of Al-doping Suggests Improved Cycling Stability





- Improved cycling stability of Al-doped NMC76 polycrystalline are observed in both half and full cell testing.
- Enhanced lattice structure stability and reduced interfacial reactions of NMC76 both help on extending the stable cycling.
- Doped NMC76 single crystals will be evaluated after synthesis optimization.

Responses to Previous Year Reviewers' Comments

- This is a new project that was not reviewed last year.

Collaboration and Coordination with Other Institutions

- Brookhaven National Laboratory: XRD characterization and structural analysis (This is a new project that started in 2019. More collaboration will be sought based on progress need.)

Remaining Challenges and Barriers

- The rate capability of single crystal cathode is expected to be lower than polycrystalline, but there is always a balance between energy and power in realistic batteries.

- Probing the global interfacial information of the entire cathode.

Proposed Future Work

- Further improve the reversible capacity of NMC76 single crystal to be close to its crystalline counterpart.
- Further validation of doping/coating effects in thick electrodes.
- Investigate the failure mechanism of Ni-rich and low-Co cathodes at relevant conditions, e.g., mass loading, full cell, electrolyte content.
- Comparison of single crystal and polycrystalline NMC76 in terms of their gas generation and storage properties.

Any proposed future work is subject to change based on funding levels.

Summary

- Electrochemically active single crystalline and polycrystalline NMC76 have been successfully synthesized.
- Single crystal NMC76 delivers greater than 200 mAh/g capacity promising for building high-energy Li-ion batteries
- Thick electrodes based on single crystal NMC76 has reduced porosity and increased electrode press density without sacrificing much reversible capacity.
- Preliminary results of minor Al-doping indicate the enhanced layered structure of NMC76 while mitigating its interfacial reactions during cycling.

Acknowledgements

- DOE/EERE/VTO: Advanced Battery Research
- Team members:

Yujing Bi, Jiangtao Hu, Bingbin Wu, Linze Li, Wengao Zhao

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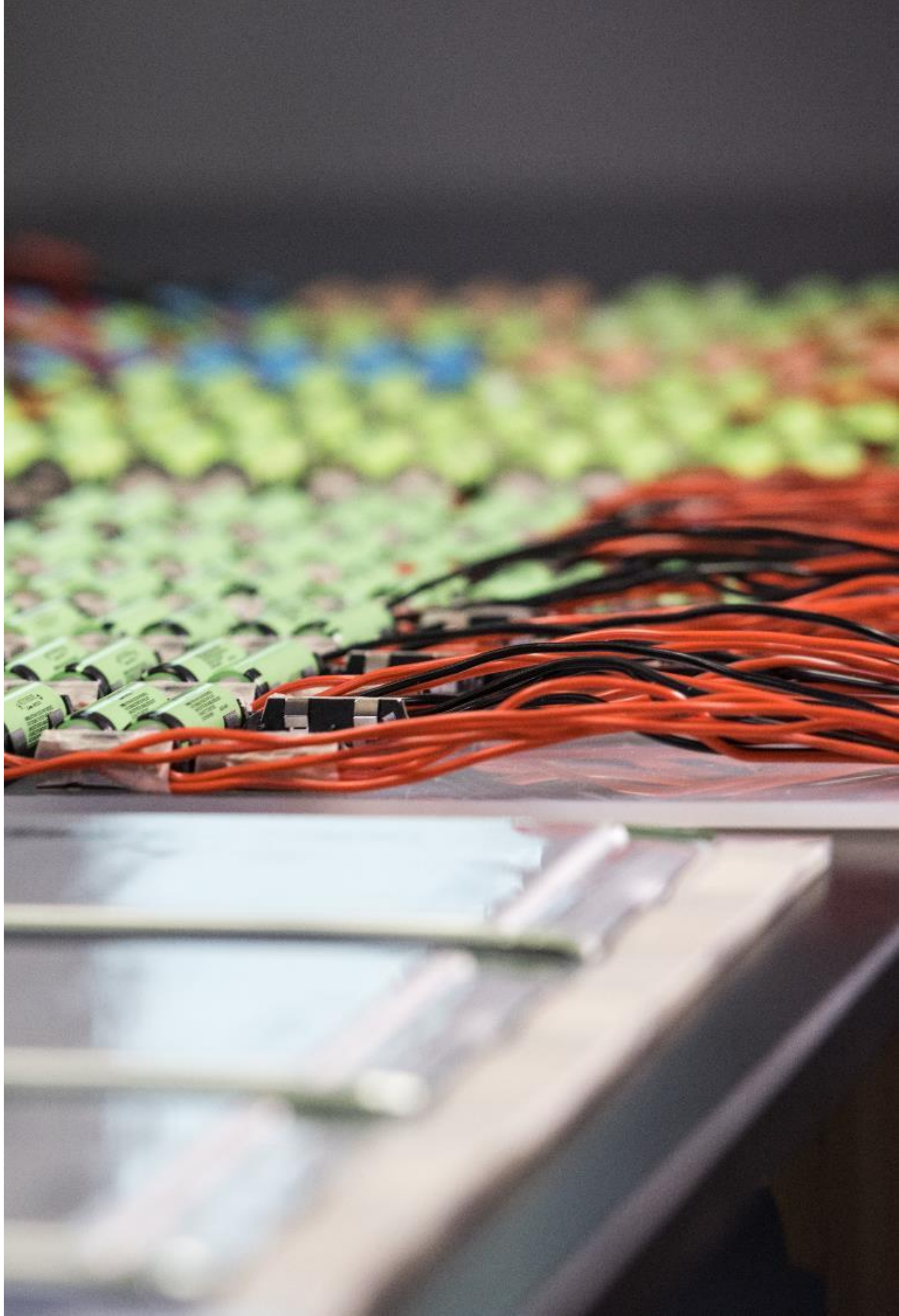
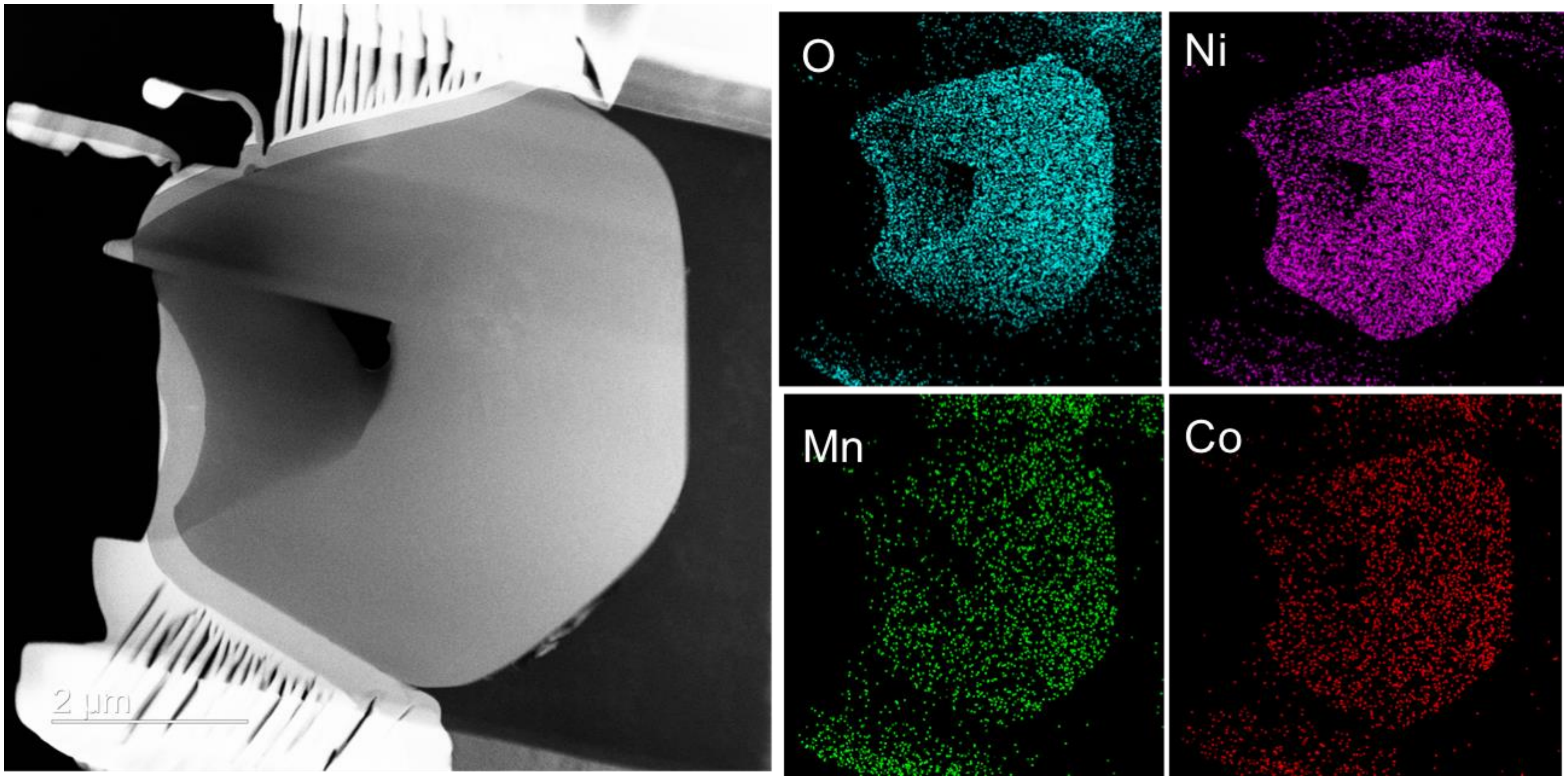
Technical Backup Slides



250 Wh/kg Cell Design Based on Graphite-NMC76 Chemistry

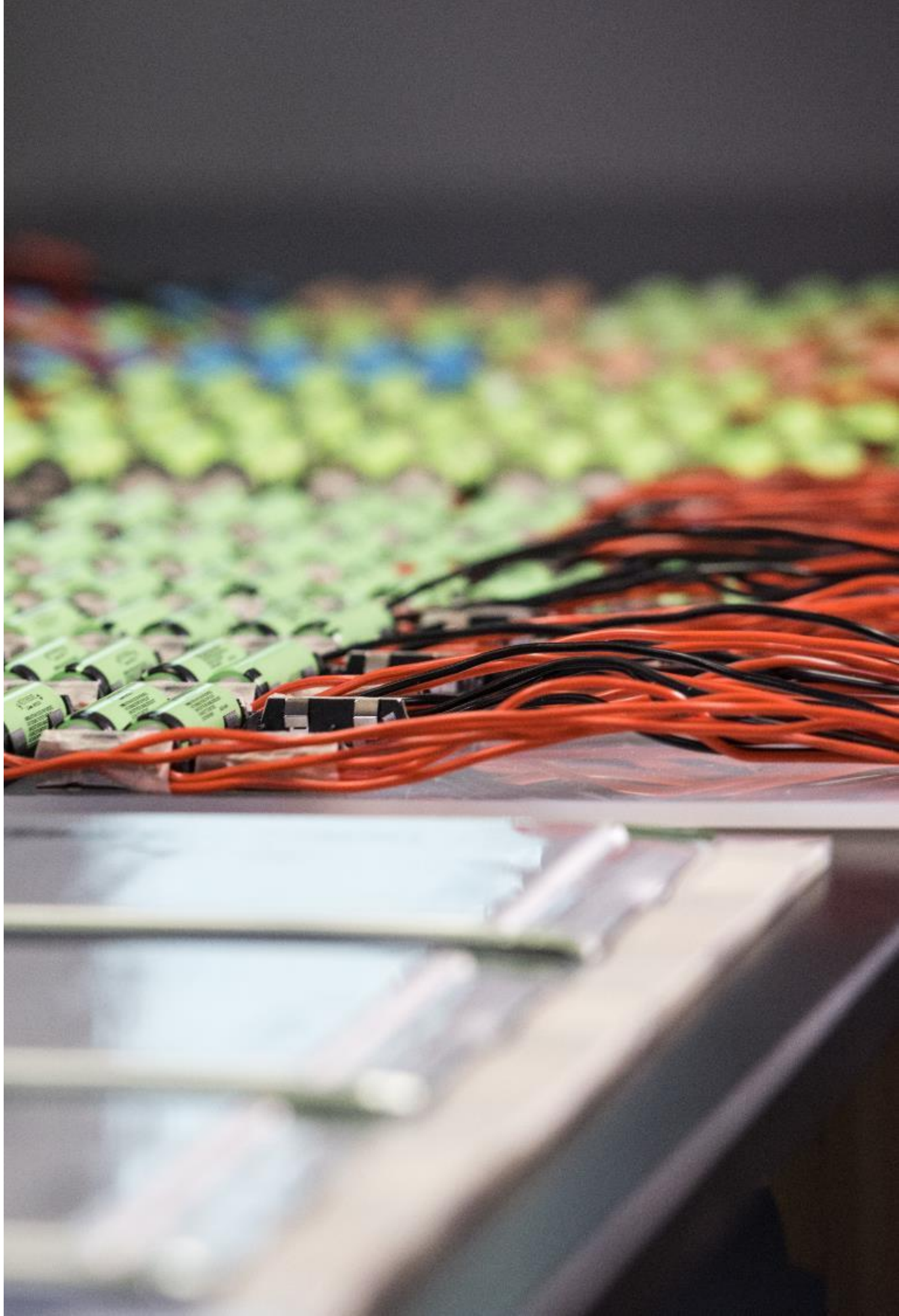
Cathode	Material	$LiNi_{0.76}Mn_{0.14}Co_{0.1}O_2$
	1st discharge capacity / mAh g^{-1}	200
	Active material Loading	96%
	Coating weight (each side) / mg cm^{-2}	21
	Areal capacity (each side) / mAh cm^{-2}	4.0
	Electrode press density / g cm^{-3}	3.0
	Electrode thickness (each side) / μm	70
	Number of double side Layers	13
	Electrode dimension W*L / mm	36*54
Al foil	Thickness / μm	12
Anode	Material	Gr.
	Specific capacity / mAh g^{-1}	360
	Active material Loading	96%
	N/P ratio (cell balance)	1.16
	Coating weight (each side) / mg cm^{-2}	13.5
	Electrode dimension W*L / mm	37.5*55.5
Cu foil	Thickness / μm	8
Electrolyte	E/C ratio / g Ah^{-1}	2.5
Separator	Thickness / μm	20
Packet Foil	Thickness / μm	88
Cell	Average voltage (1st cycle) / V	3.65
	Capacity (1st cycle) / Ah	2.0
	Cell Energy / Wh kg^{-1}	**250**

TEM Confirms the Absence of Grain Boundaries in NMC76 Single Crystals



- STEM image shows single-crystalline structure without grain boundaries.
- EDS results show uniform composition distribution throughout the particle.

Reviewer Only Slides



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Publications and Presentations

This is a new project started in FY2018.

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Critical Assumptions and Issues

- Single crystalline generally delivers lower capacity compared to polycrystalline. After further synthesis modification, it is expected that single crystal Ni-rich cathode will deliver capacity close to its polycrystalline counterpart.

- Single crystalline will mitigate the issues of gassing and particle “cracking” along grain boundaries during cycling. The safety and long-term storage and cycling stability of Ni-rich cathode materials will be improved by using single crystalline Ni-rich cathode.